91600
new 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if Reproduced in Whole or in Part.

ontario hydro
research division

EXECUTIVE SUMMARY

DETERMINATION OF GROSS GAMMA AND GROSS BETA ACTIVITIES IN LIQUID EFFLUENT SAMPLES - PHASE I

K.E. Curtis and S.P. Sood
Chemists
Analytical Services Section
Chemical Research Department

Gross gamma and gross beta measurements are used by Ontario Hydro's nuclear stations for monitoring active liquid effluents before they are released to the environment. Large discrepancies have been observed between the activities measured by the two procedures with the gross beta method giving much lower results than the gross gamma analysis. Several parameters that could cause such a discrepancy were identified and have been investigated in this study. Storage of neutral or slightly basic samples in polyethylene bottles for at least one month did not cause significant losses of activity from solution but losses of radioiodine occurred in acidified solutions that were left unsealed for more than a few minutes. Gross gamma measurements were found to overestimate the activity in samples containing suspended particulate activity and the use of a cesium-137 standard for calibration in this technique also caused a positive bias. At the same time, large losses of volatile radionuclides such as iodine-131 were found to occur during sample preparation for gross beta determinations, especially in acidic solutions. Low results for these measurements were also obtained unless the quantity of total suspended and dissolved solids in the sample was taken into account. A combination of these potential sources of error could result in discrepancies of a similar order of magnitude to those observed during actual sample analysis.

job	file	date	report no.
740633-203-592 740633-523-592	837.39	August 22, 1985	85-238-K

91600
new 82-10

ontario hydro
research division

To Mr. R.T. Popple
Manager
Radioactive Management and
Environmental Protection

DETERMINATION OF GROSS GAMMA AND GROSS BETA ACTIVITIES IN LIQUID EFFLUENT SAMPLES - PHASE I

K.E. Curtis and S.P. Sood

Several inadequacies in the presently used procedures for gross gamma and gross beta measurements in aqueous wastes have been identified. Both the presence of suspended particulate activity and the use of cesium-137 as a calibration standard can cause gross gamma measurements to overestimate the actual activity in the sample. At the same time, sample preparation for the determination of gross beta activities causes large losses of radioiodine before the measurement step and the presence of solid material can cause a serious decrease in the beta counting efficiency. A combination of these errors could result in large discrepancies between the results obtained by the two measurement methods. Improved procedures are required to overcome these problems.

1.0 INTRODUCTION

The policy of Ontario Hydro is to operate nuclear generation facilities in such a manner that radiation exposure to the general public does not exceed limits specified by the Atomic Energy Control Board of Canada (AECB). To meet the objectives of minimizing radiological emissions to as low as reasonably achievable, the operating target has been set at 1% of the Derived Emission Limit (DEL)/1/. All the effluent streams which could potentially contribute enough radioactive material to exceed the target value are monitored and standards for a monitoring program have been set/2/. The basic requirements for monitoring liquid waste effluents include gross beta (excluding tritium which is

job	file	date	report no.
740633-203-592 740633-523-592	837.39	August 22, 1985	85-238-K

measured separately) or gross gamma analysis for control as well as compliance monitoring. All nuclear generating stations have such a monitoring program for their liquid effluents and both gross beta and gross gamma measurements are performed. These measurements indicate the total number of Curies of activity of all suspended and dissolved radionuclides other than tritium in the effluent streams. Large discrepancies have been observed between some gross beta and gross gamma analyses which led to an initial investigation at Douglas Point NGS/3/. Generally, gross beta activities were found to be lower than corresponding gross gamma measurements by a factor of between 30 and 40. At the request of the Radioactivity Management and Environment Protection Department (RMEP), a project was initiated at the Chemical Research Department to assess the accuracy of the different procedures used at the stations and to determine the source of any errors.

2.0 RADIONUCLIDES IN LIQUID EFFLUENTS FROM A NUCLEAR GENERATING STATION (NGS)

During the operation of a NGS the radionuclides generated are the products of the fission of uranium and the neutron activation products of the coolant, moderator, structure and fertile materials and gases in the reactor. Fission products are contained within the fuel cladding and are discharged from the reactor along with the spent fuel. However, any cladding failure releases small quantities of these radionuclides to the primary heat transport (PHT) system. The activation of heavy water produces tritium in the moderator and PHT liquid. Carbon-14 is produced from activation of carbon-13 and nitrogen-14 (N-14 (n,p) C-14) and may be present in the inorganic or organic form in the liquid streams. The corrosion of materials leads to the release of neutron activation products to the liquid streams. Discharge of these radioactive streams by any means results in the radioactive liquid waste. The average composition, as determined by gamma spectrometry, of typical radioactive liquid wastes from Pickering NGS and Bruce NGS "A" is shown in Table I/4/.

3.0 MONITORING OF TOTAL QUANTITY OF RADIOACTIVITY RELEASED THROUGH LIQUID EFFLUENTS

3.1 Tritium and Carbon-14

Tritium and carbon-14 are pure low energy beta emitters. Tritium is measured using standard liquid scintillation counting. Carbon-14 is distilled as carbon dioxide, absorbed in a special liquid scintillation cocktail and counted by the standard technique/5/.

3.2 Gross Beta and Gross Gamma Measurements

A NaI(Tl) detector is employed for the gross gamma measurements. This provides a higher counting efficiency but much less energy resolution than are obtained with a germanium detector. The gamma spectrometer registers an energy spectrum and all the events in

TABLE I

RELATIVE AVERAGE RADIONUCLIDE ABUNDANCE IN WASTE TANKS (%)

Radionuclide	Half-Life	PNGS-A	BNGS-A
Chromium-51	27.8 d	11	24
Manganese-54	303 d	-	<1
Iron-59	45 d	1	1
Cobalt-60	5.26 y	25	7
Zinc-65	244 d	1	<1
Niobium-95	35 d	1	7
Zirconium-95	65 d	1	4
Ruthenium-103	39.6 d	1	1
Ruthenium-106	369 d	2	6
Cadmium-109	450 d	-	1
Antimony-124	60 d	-	2
Antimony-125	2.7 y	-	4
Iodine-131	8 d	19	3
Xenon-133	5.3 d	4	-
Cesium-134	2.1 y	4	7
Cesium-136	13 d	1	-
Cesium-137	30 y	16	19
Barium-140	12.8 d	2	-
Cerium-141	33 d	1	1
Cerium-144	284 d	2	7
Gadolinium-153	242 d	-	3
Europium-154	16 y	-	<1
Mean Tank Activity (nCi/L)		2.1	27

the energy interval of 100 to 2000 keV are integrated. It also allows identification of the major radionuclides if present in sufficient quantities. The method is fast and is easily adapted to continuous control monitoring. However, it is relatively insensitive with a minimum detectable activity (MDA) of 100 pCi/L.

Gross beta measurements on the other hand have a much better sensitivity with a MDA of 2 pCi/L. A gas flow proportional counter with or without a window is used to quantify total beta emitting radioisotopes. However, the method is very slow and requires several hours for sample preparation. It is also sensitive to the sample preparation technique used (eg, loss of volatile radionuclides), the solid content of the sample and does not identify individual radioisotopes. If identification of the beta emitters is desired, a time consuming chemical separation procedure is necessary. Being slow, the method does not lend itself to continuous control monitoring. However, it is regularly employed for batch emission monitoring and compliance monitoring due to its good sensitivity.

For calibration of the detectors for gross beta and gross gamma measurements, when the expected source is a mixture of radionuclides, a certified standard solution of cesium-137 is used.

4.0 LIQUID EFFLUENT SAMPLING AND SAMPLE PREPARATION

One of the important phases of liquid effluent monitoring is the establishment of acceptable procedures for sampling and sample preparation such that a representative value for the quantity of radioactivity in the stream can be obtained. General guidelines for sampling parameters such as location, frequency, duration, volume, flow and composition have been established/2/. Sample preparation prior to the actual measurements of the activity in the effluent for compliance monitoring may be required. As few steps as possible are desired in the preparation of the samples to reduce costs, the possibility of cross-contamination and sample processing errors.

The preparation of effluent samples for analysis suffers from a number of problems for which well-defined answers are not available. These problems are due to non-homogeneity of the sample (presence of insoluble material), the behavior of substances at very low concentrations which is unpredictable and poorly understood (colloid formation, deposition on suspended solid and/or on the wall of the container) and the presence of volatile radionuclides. Filtration and/or acidification may be the commonly used initial steps in preparation prior to further processing. This may take the form of:

(a) Chemical separation (eg, separation of carbon-14 from other radionuclides before liquid scintillation counting, strontium-90 separation and measurements and separation of alpha emitters from sample matrix to improve sensitivity and accuracy).

(b) Physical separation operations without any chemical processing (eg, making a composite sample, concentration to reduce volume or evaporation to dryness).

The chemical separations are in general time consuming and hence their use is limited to cases where it is essential that the concentration of specific species be determined. The physical operations are, however, quite routine in sample preparation to ensure uniform distribution of radioactive substances. Sample homogeneity becomes more important as the range of the radiation becomes shorter or for larger samples used for low-level gamma ray counting. The detector geometry (efficiency) may vary for sources of radiation in different parts of large non-homogeneous samples.

A variety of sample preparation techniques are employed in Ontario Hydro and are listed in the Appendix/6/. The objective of Phase I of the present study is to evaluate the importance of various parameters in the sample preparation procedure and their effects on the final results of analysis.

5.0 PROCEDURES AND RESULTS OF EXPERIMENTS

The following parameters which could influence the reliability of the gross beta-gamma measurements were studied:

(a) Presence of activity in the particulate form,

(b) Loss of activity during storage periods of up to 2 months,

(c) Activity of strontium-90 in liquid effluent samples,

(d) Influence of the total dissolved and suspended solids on the counting efficiency for gross beta measurements,

(e) Loss of activity during sample preparation.

5.1 Effect of Active Suspended Material on Gross Gamma Measurements

5.1.1 Preparation of Sample

Approximately 1 mg of crud with a total activity of about 2 uCi and having the following major radionuclide composition

Cobalt-60	58.7%
Cerium-144	23.2%
Ruthenium-106	16.7%
Niobium-95	1.4%

was placed in a 100 mL beaker along with 40 mL of tap water. It was subjected to ultrasonic dispersion for four hours. The suspension was allowed to settle for 15 minutes in order to eliminate the faster settling particulate aggregate and then the

supernatant suspension was carefully separated and diluted to one liter with tap water in a polyethylene bottle.

5.1.2 Gamma Activity Measurements

The sample bottle was well shaken and placed on a germanium detector coupled to an ORTEC Series 7052 Data Acquisition and Analysis system and counted immediately and after various settling intervals. A fixed geometric calibration was used to measure the activities of various radionuclides.

5.1.3 Results and Discussion

The variation in the total measured activity of the sample relative to the initial value, A(t)/A(o), with settling time is shown in Figure 1. The variation in the apparent activity of the individual radionuclides is listed in Table II. It can be seen from Figure 1 that even for a short settling period of one hour, there was a considerable increase in the measured gamma activity, of about 80%. This apparent activity continued to increase significantly until 24 hours after the initial measurement but was then relatively constant over the rest of the period of observation. The apparent activity was a factor of about four higher than the actual activity at this stage. A similar variation in the activities of the individual radionuclides was also observed indicating that there was no preferential leaching of any of the radionuclides originally present in the crud during the dispersion or storage. After a settling period of 4 days the bottle was reshaken and counted. The measured activities returned to their original values.

This variation in the A(t)/A(o) ratio shown in Figure 1 is an extreme example where all the activity is in suspension. However, it clearly shows that active particulate matter can contribute to a significant positive bias in gross gamma measurements if sufficient care is not taken to ensure that the sample is well mixed before counting.

5.2 Effect of Storage Period on the Measured Activity

5.2.1 Preparation and Storage of Samples

A small quantity of crud with approximately 2 uCi of total activity was digested in concentrated hydrochloric acid in a 50 mL beaker for four hours. The contents of the beaker were then taken to almost dryness and diluted to 500 mL with distilled water in a 1 L beaker. Just enough ammonium hydroxide was added to precipitate the iron in the sample. The solution was filtered to remove suspended material and the filtrate was then mixed with 200 mL of PHT liquid and diluted to 10 liters with tap water. The pH of the resulting solution was adjusted to 7 and 20 uCi of iodine-131 was added to it. The solution was then well mixed and 1 liter of it was placed into each of 10 polyethylene bottles. Five were preserved by the addition of 5 mL concentrated nitric acid and

TABLE II

EFFECT OF SETTLING TIME ON MEASURED RADIONUCLIDE ACTIVITY

DECANTATION TIME (h)	ACTIVITY (uCi/L)			
	Co-60	Ce-144	Ru-106	Nb-95
0	1.00	0.34	0.30	0.043
1	1.79	0.67	0.48	0.044
6	2.84	1.16	0.68	0.074
24	4.03	1.58	1.05	0.093
30	3.99	1.63	1.03	0.108
48	4.12	1.63	1.17	0.100

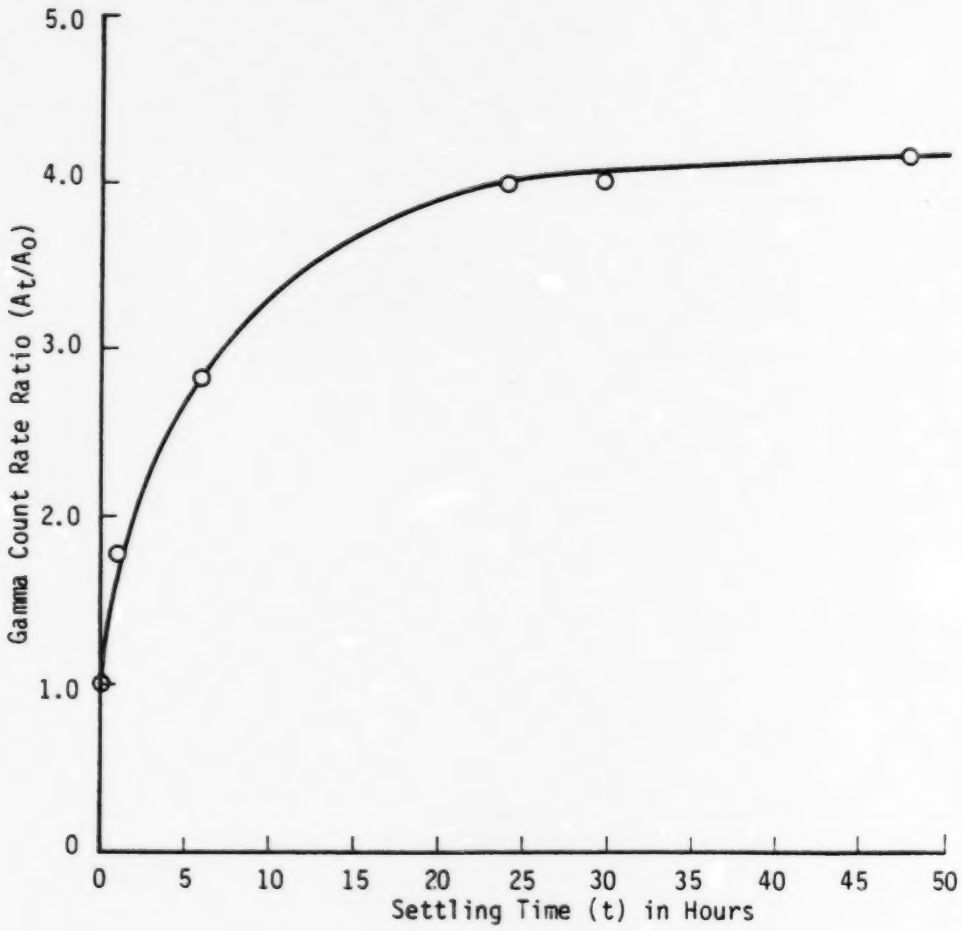


FIGURE 1

EFFECT OF SETTLING TIME ON RELATIVE GAMMA COUNT RATE

were stoppered immediately, mixed and labelled for storage. The other 5 bottles were stoppered without any preservation and labelled. All ten solutions were analyzed by gamma spectrometry and found to have the following relative distribution of activity:

Cobalt-60	5.7%
Cesium-134	1.8%
Cesium-137	5.7%
Iodine-131	84.8%
Niobium-95	0.1%
Ruthenium-106	1.2%
Antimony-125	0.6%

Each of the bottles contained approximately 20 uCi of tritium, 1 uCi of total gamma activity and 0.2 nCi of strontium-90. The bottles were arranged in five pairs, each pair consisting of a bottle containing a neutral solution and the other an acidified solution. They were stored undisturbed until used.

5.2.2 Sample Treatment and Counting

After a desired time interval, a pair of bottles was retrieved from storage and 500 mL of the solution from each bottle was carefully poured out into separate 600 mL beakers, without any shaking. They were sealed with a plastic film and counted on a germanium detector as described in Section 5.1.2.

5.2.3 Results and Discussion

All of the activities were decay corrected to the time of sample preparation and then ratioed to the originally-measured activities for the particular sample. The results are listed in Table III.

It should be noted that an unrealistic excess of iodine-131 was added to the initial stock solution so as to have some activity left after a long storage period. Having a half-life of only 8 days, less than 1% of the original iodine-131 activity remained after 8 weeks of storage. A large decay correction was therefore necessary, magnifying any uncertainty in the actual activity measurement. The measured activities of some of the other radionuclides have large uncertainties associated with low count rates.

It can be seen from these results that there was little if any loss of activity during storage periods of up to 8 weeks in neutral solution. However, in acidic medium, a slight loss of activity of cobalt and cesium isotopes was noticed after 8 weeks of storage. This is quite contrary to the general observation that acidification prevents losses due to adsorption on the walls of the containers during storage. A drift in the electronics of the counting equipment is suspected to be the cause of this deviation rather than actual losses of activity.

TABLE III

EFFECT OF THE STORAGE TIME

Radio-nuclide	Per cent Original Activity (Decay Corrected to the Day of Preparation of the Stock Solution)									
	Same Day		After 1 Week		After 2 Weeks		After 4 Weeks		After 8 Weeks(b)	
	pH <2	pH = 7	pH <2	pH = 7	pH <2	pH = 7	pH <2	pH = 7	pH <2	pH = 7
Co-60	97 ±5	96 ±5	94 ±5	94 ±5	96 ±5	95 ±5	93 ±5	93 ±5	91 ±5	97 ±5
Cs-134	102 ±6	96 ±6	98 ±6	98 ±6	96 ±6	99 ±5	97 ±6	98 ±5	76 ±6	98 ±5
Cs-137	93 ±5	95 ±5	97 ±5	100 ±5	99 ±5	100 ±5	82 ±5	83 ±5	70 ±5	102 ±5
I-131	52 ±5(a)	98 ±5	91 ±5	97 ±5	89 ±5	97 ±5	90 ±5	95 ±5	124 ±7(b)	96 ±6(b)
Nb-95(c)	154 ±62	77 ±36	122 ±50	87 ±34	65 ±30	81 ±30	119 ±50	60 ±24	47 ±50	119 ±30
Ru-106(c)	103 ±36	85 ±30	115 ±40	108 ±26	102 ±33	114 ±29	93 ±30	73 ±24	93 ±16	94 ±26
Sb-125(c)	98 ±34	100 ±30	92 ±30	78 ±37	111 ±30	135 ±35	109 ±30	115 ±28	102 ±10	106 ±24

(a) Sample left unsealed in the fumehood for 2 hours before counting.

(b) Large decay corrections are needed for iodine-131.

(c) Large counting uncertainties in these measurements due to low count rates.

There appears to be a consistent low bias in the iodine-131 recoveries in the acidified solutions, suggesting a constant loss of this radionuclide during the transfer of the acidified samples to the beaker. This loss can be significant if the solution is left unsealed for any extended period of time, as shown by the first value given for iodine in Table III and marked with the Note (a).

It can be concluded from these data that storage for up to 4 weeks, the time needed to collect a monthly composite sample, of filtered neutral solution does not result in any significant loss of activity. Loss of radioiodine from an acidified solution can be expected if it is left unsealed for more than a few minutes.

5.3 Strontium-90 Activity in Liquid Effluent Samples

5.3.1 Background Information

Strontium-90 and its daughter product, yttrium-90, are pure beta emitters and are not measured during gross gamma determinations. The only data on their activities in liquid effluent samples were reported in 1976/7/ as 140 pCi/L for one sample from Pickering NGS and 180 pCi/L for one other sample from Douglas Point NGS. Arrangements were therefore made to obtain additional samples from both Pickering NGS and Bruce NGS "A". Also of interest was the measurement of the cesium-137/strontium-90 activity ratios.

5.3.2 Experimental Procedure

Only two 2 L samples were received for analysis from Pickering NGS. They were analyzed for strontium-90 activity using a previously developed procedure/8/ that isolates the strontium-90 (or at least its daughter product, yttrium-90) from all other radionuclides in the sample before its activity is measured.

5.3.3 Results and Discussion

The strontium-90 activities were found to be 100 $\pm$40 pCi/L for the July, 1983 sample and 180 $\pm$100 pCi/L for the August, 1983 sample, in general agreement with the previous results. The high uncertainties in the data are due to a relatively high background count rate compared to the sample count rates. New counting equipment has since been purchased and set up in a low level laboratory for future low activity measurements of this type.

The corresponding cesium-137 activities for the two samples were 1100 $\pm$15 pCi/L and 790 $\pm$20 pCi/L, giving cesium-137/strontium-90 activity ratios of 11 and 4.4 respectively. These ratios do not agree well with the theoretical figure of 1.5 but are closer to that value than the previously reported estimates of >100 and 200/7/.

5.4 Effect of Sample Thickness on the Counting Efficiencies of Gross Beta and Gross Gamma Measurements

5.4.1 Experimental Procedure

An aliquot of a standard solution of cesium-137 was deposited on a weighed planchet and was evaporated to dryness and reweighed. There was no observable change in the weight of the planchet and this was counted as a zero thickness source for gross beta on a PC-5 detector, and for gross gamma on a NaI(Tl) detector coupled to a Canberra Series 30 Multichannel Analyzer in the region of 100 to 2000 keV. The background count rates for both the detectors under similar conditions were also determined and subtracted to obtain the net counts.

An alkaline phosphate/hydrazine reagent consisting of 5 g of NaOH, 50 g of $Na_3PO_4.12\ H_2O$ and 10 mL of 35% v/v N_2H_4 solution diluted to one liter with distilled water was prepared. This reagent was previously recommended for sample preparation for gross beta measurements/1/ and is currently used in the Pickering NGS procedure (see Appendix).

An 0.5 mL aliquot of this reagent was mixed with 500 mL of tap water and evaporated to approximately 10 mL. The resulting slurry was transferred to the weighed planchet containing the zero thickness cesium-137 deposit and then evaporated to dryness. It was then reweighed and counted for both gross beta and gross gamma activities.

Further amounts of solid material (160 mg and 150 mg of ammonium sulfate, respectively) were then added to the planchet in 0.5 mL portions of tap water. After each addition, the planchet was again evaporated to dryness, weighed and counted as before.

5.4.2 Results and Discussions

The variation in the ratio of the net count rate of the sample having a sample weight w, A(w), and the source with zero thickness, A(o), with the source weight is shown in Figure 2 for both gross beta and gross gamma measurements. As expected, there was little variation in the gross gamma values except for a slight decrease compared to the zero thickness source. This is probably due to changes in the geometry of the sample caused by the presence of the solids. Gross beta measurements, however, were significantly affected by the solid material on the planchet and the resulting attenuation of the emitted beta particles. At a solid content of 100 mg, considered typical for a 500 mL sample containing 0.5 mL of the alkaline phosphate reagent, the activity was underestimated by 33%. The further additions of solid material gave apparent activities that were lower than the actual activity by factors of about 2 and 3, demonstrating the need for correction factors when making gross beta measurements on samples containing variable quantities of solid material. This is in fact included

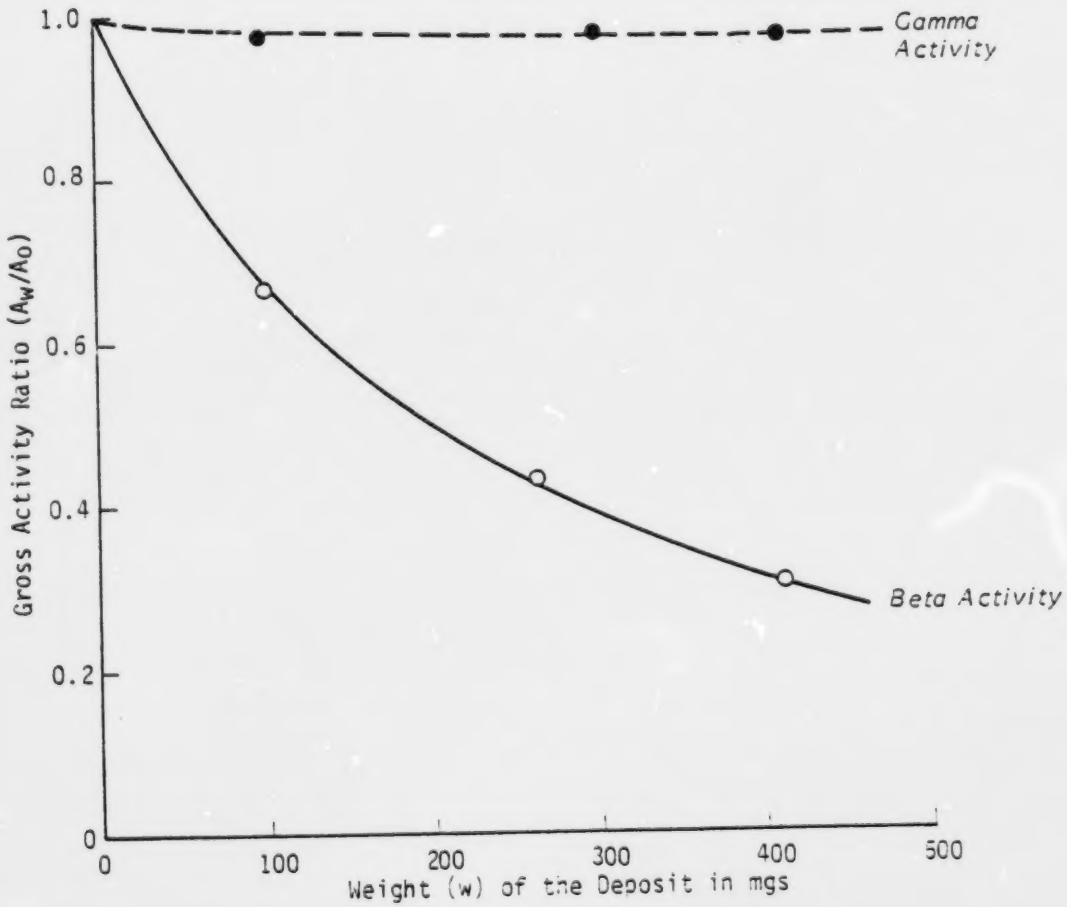


FIGURE 2

VARIATION IN THE GROSS BETA AND GROSS GAMMA COUNTING EFFICIENCY WITH SOURCE THICKNESS FOR A CESIUM-137 STANDARD

in the procedures used by BNPDS Health Physics and Central Safety Services (see Appendix).

5.5 Loss of Activity During Sample Preparation

Basically two sample preparation techniques have been employed at nuclear generation stations in Ontario Hydro, namely, evaporation in the presence of nitric acid (BNPDS Health Physics laboratory for BNGS-A and DPNGS and at CSS for NPD) and evaporation in the presence of the alkaline phosphate/hydrazine reagent, as at PNGS-A (see Appendix). Both these sample preparation techniques were evaluated by using synthetic mixed radionuclide solutions.

5.5.1 Experimental Procedure

5.5.1.1 Sample Preparation in the Presence of Nitric Acid

Four 500 mL solutions prepared as described in Section 5.2.1 were acidified to a pH of 1.1 by the addition of 2.5 mL of concentrated nitric acid. Each solution contained approximately 0.5 uCi of total gamma activity, distributed as shown in Section 5.2.1. The samples were counted to determine their actual starting specific gamma activities and were then evaporated to about 10 mL and recounted. The contents of each beaker were carefully transferred to separate preweighed stainless steel planchets (5.1 cm diameter with an 0.5 cm lip) and then evaporated to dryness under a heat lamp. The planchets were reweighed and counted for specific gamma, gross gamma and gross beta activities.

5.5.1.2 Sample Preparation with the Alkaline Phosphate Reagent

Four neutral 500 mL solutions were prepared as described in Section 5.2.1, except that varying amounts of iodine-131 were added to each solution to give the relative activity composition shown in Table IV. The total gamma activities of these solutions ranged from 0.1 to 0.5 uCi, depending on the quantity of iodine-131 added. An 0.5 mL aliquot of the alkaline phosphate/hydrazine reagent was added to each solution and they were then treated as described above in Section 5.5.1.1.

5.5.2 Results and Discussion

5.5.2.1 Acidified Solutions

Although the recoveries of the major radionuclides such as cobalt-60 and cesium-137 in these solutions were better than 90%, about half of the iodine-131 was lost during the evaporation to 10 mL and the remainder was lost during the transfer to the planchet and subsequent heating to dryness. Significant losses of antimony-125 were also observed. Since iodine-131 can constitute a considerable fraction of the total activity in liquid wastes (see Table I), the acidified solution procedure was rejected as unsuitable and was not studied further.

TABLE IV

LOSS OF ACTIVITY DURING SAMPLE PROCESSING
WITH THE ALKALINE PHOSPHATE/HYDRAZINE REAGENT

Sample #	Step in Procedure	Per cent of Initial Activity Remaining			
		Cobalt-60	Cesium-134	Cesium-137	Iodine-131
	Relative Activity Composition	6.3%	2.0%	5.9%	85.8%
1	500 mL Alq.	100	100	100	100
	Evap. 10 mL	113 ±6	111 ±6	116 ±6	82 ±4
	On Planchet	92 ±5	93 ±5	106 ±6	44 ±2
	Relative Activity Composition	10.2%	3.2%	9.7%	76.9%
2	500 mL Alq.	100	100	100	100
	Evap. 10 mL	113 ±6	108 ±6	116 ±5	47 ±3
	On Planchet	99 ±5	96 ±6	111 ±6	29 ±2
	Relative Activity Composition	15.6%	4.9%	14.8%	64.6%
3	500 mL Alq.	100	100	100	100
	Evap. 10 mL	101 ±5	97 ±5	100 ±6	76 ±5
	On Planchet	94 ±6	93 ±6	108 ±6	55 ±4
	Relativ Activity Composition	29.4%	9.2%	23.5%	37.9%
4	500 mL Alq.	100	100	100	100
	Evap. 10 mL	107 ±6	102 ±6	127 ±7	85 ±5
	On Planchet	96 ±5	94 ±5	127 ±7	64 ±4

5.5.2.2 Alkaline Phosphate Reagent Procedure

The fraction of the initial activity remaining after evaporation to 10 mL and then after transferring to the planchet and drying are shown in Table IV. There was little loss of the cobalt and cesium radioisotopes during concentration to 10 mL but iodine was lost to a varying degree, between 15 and 50%. Recoveries of greater than 100% are most likely due to counting geometry effects resulting from differences in the beakers used for calibration and sample processing.

During the transfer and drying steps the recovery of the cobalt and cesium radionuclides was again better than 90%. However, losses of the radioiodine continued to occur at about the same rate as during the evaporation step. The average total loss of iodine-131 activity was about 50%, in agreement with results from previous preliminary tests with this reagent/9/.

Although the use of the alkaline phosphate/hydrazine reagent reduces the iodine-131 losses during sample preparation, it still must be considered unacceptable if that radionuclide is present in any significant quantity. The next phase of this work should include an investigation of a new method of preventing such losses.

5.6 Comparison of Activities Measured by Gross Beta, Gross Gamma and Specific Gamma Counting

5.6.1 Sample Preparation and Counting

The four planchets prepared in Section 5.5.1.2 were counted for gross beta, gross gamma and on a germanium detector to determine their specific gamma composition, as described previously in Sections 5.1.2 and 5.4.1. Each gross beta measurement was corrected for the quantity of solid material found on the planchet and the activities obtained by each of the three counting methods were compared.

5.6.2 Results and Discussion

The weight of the solids on the four planchets was 260 $\pm$10 mg and therefore the counting efficiency determined with 260 mg of solid on the standard cesium-137 source (see Section 5.4) was used to determine the gross beta activities. The results of all three measurement methods are presented in Table V and it can be seen that the gross beta measurements agree quite well with the specific gamma measurements, although the gross beta value for sample number 1 shows a slight positive bias. Gross gamma measurements show a significant positive bias in all cases indicating that calibration with cesium-137 which has less than one gamma ray emission per disintegration cannot be satisfactorily used for other radionuclides which have more than one gamma emission per disintegration, such as cobalt-60 and cesium-134.

TABLE V

MEASUREMENT OF SAMPLE ACTIVITY USING GROSS BETA, GROSS GAMMA AND SPECIFIC GAMMA COUNTING

Sample #	Total Activity from Sum of Specific Gamma Activities (nCi)	Activity from Gross Beta Counting (nCi)	Activity from Gross Gamma Counting (nCi)
1	82 ±4	96 ±4	104 ±5
2	78 ±4	82 ±4	103 ±5
3	83 ±4	86 ±4	118 ±6
4	87 ±4	86 ±4	111 ±5

The strontium-90 activity in these samples was only 0.1 nCi and therefore was not of any significance in these synthetic samples.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Suspended particulate activity can cause gross gamma measurements to overestimate the actual sample activity unless the sample is well mixed immediately before counting and relatively short counting times are used.

6.2 Neutral or slightly basic samples collected for either gross gamma or gross beta determinations can be stored in polyethylene bottles for at least four weeks without significant loss of activity. Losses of iodine-131 occur in acidified solutions if the samples are left unsealed for more than a few minutes and during decantation of the sample from the storage bottle.

6.3 The average strontium-90 content of two liquid effluent samples from Pickering NGS was found to be about 140 pCi/L, in agreement with previously determined values/7/. This level of activity should not cause any serious discrepancies between gross gamma and gross beta analyses.

6.4 The counting efficiency for gross beta measurements is significantly decreased by increasing amounts of suspended and dissolved solids in the sample. Correction factors are required to compensate for this effect. Gross gamma measurements are relatively unaffected by this parameter.

6.5 All of the gross beta sample preparation procedures used by Ontario Hydro result in large losses of radioiodine activity before the measurement step. The loss is total in acidified solutions while the use of a recommended alkaline phosphate/hydrazine reagent/1/ reduces the loss by only 50%. Either a new reagent or a totally new sample preparation procedure is required for the determination of gross beta activities of samples containing significant quantities of radioiodine.

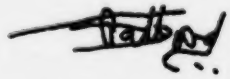
6.6 Measurement of the activity of samples prepared on planchets showed the gross beta results, corrected for solid material content, to agree well with the sum of the specific gamma activities. Gross gamma results showed a positive bias of about 30%, suggesting that the use of a cesium-137 standard for calibration is not acceptable for gross gamma counting of samples containing a mixture of normal fission and activation products.

6.7 The above findings show that for a sample containing significant activities of suspended particulate matter and dissolved radioiodine, the gross gamma measurement can overestimate the actual activity while the gross beta

determination will be biased low. This could result in a discrepancy between the two results of at least an order of magnitude.

6.8 Phase II of this work should include an investigation of new reagents for fixing the radioiodine activity in the sample, alternative calibration techniques for gross gamma determinations and an improved, less time consuming sample preparation procedure for gross beta measurements.

Prepared by:

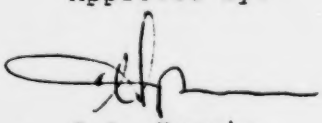


K.E. Curtis
Chemist - Analytical Methods
Analytical Services Section

and

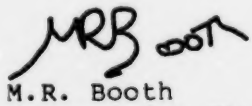
S.P. Sood
Chemist - Analytical Nuclear
Analytical Services Section

Approved by:



O.A. Kupcis
Manager
Chemical Research Department

Reviewed by:



M.R. Booth
Supervising Chemist
Analytical Services Section

KEC/SPS:mf

REFERENCES

1. Wong, K.Y., "Liquid Effluent Monitoring," Health and Safety Division Recommended Radiological Practice 6.6, July, 1974.

2. Maruska, R., "A Proposed NGD Policy and Standard for the Monitoring of Radioactivity in Liquid Effluents," Report No RMEP-IR-03442-1, July, 1982.

3. Vanderzwet, F., "Comparison of Gross Beta and Gross Gamma in Liquid Samples," Report No DP-IR-678-2, May, 1982.

4. Brennenstuhl, K.R., personal communication.

5. Curtis, K.E., "Determination of Carbon-14 in Aqueous Waste," Research Division Report No 81-407-K.

6. Brennenstuhl, K.R., "Gross Beta Gamma Liquid Effluent Emissions," memorandum to M.R. Booth on May 2, 1983.

7. Wong, K.Y. and McKenzie, K., "Radiochemical Studies of Radio-Strontium and Alpha Activities in CANDU System Water Samples," Report No HPD-76-2, January, 1976.

8. Curtis, K.E., "Determination of Strontium-90," Research Division report No 82-47-K.

9. Curtis, K.E., unpublished results.

APPENDIX

SAMPLE PREPARATION TECHNIQUES EMPLOYED IN ONTARIO HYDRO

GROSS BETA SAMPLE PREPARATION AT BNPD HP LABORATORY FOR BNGS-A AND DPNGS

1. Place 400 mL sample in a glass beaker.
2. Add 5 to 10 mL nitric acid.
3. Evaporate to approximately 10 mL on hot plate close to boiling point.
4. Transfer the 10 mL to 2-inch planchet and rinse beaker with 2 to 5 mL of 25% nitric acid.
5. Evaporate under IR lamp until solid.
6. Spray lightly with lacquer and dry.
7. Determine crud weight.
8. Analyze on beta counter - 30 minutes count time.
9. Calculate results applying correction factor for weight of crud.

NOTE: The samples are received from the stations in plastic containers and with no pretreatment.

GROSS BETA SAMPLE PREPARATION AT PNGS-A

1. Place 800 mL sample in beaker.
2. Add 1 mL of alkaline phosphate/hydrazine reagent (5.0 g Na_3PO_4, 0.5 g NaOH, 1.0 g (55%) N_2H_4, demineralized water to 100 mL).
3. Evaporate on hot plate slowly overnight.
4. Count empty 2-inch planchet 200 minutes to obtain background.
5. Scrub down beaker sides with a rubber policeman. Rinse with water and evaporate to approximately 5 mL.
6. Transfer to planchet and rinse beaker thoroughly with water.
7. Evaporate to dryness under a heat lamp.
8. Analyze on beta counter - 200 minutes count time.

GROSS BETA SAMPLE PREPARATION AT CSS HP LABORATORY FOR NPD

1. Add 1 to 2 mL of 10 to 20% nitric acid to 1 L sample.
2. Evaporate to 5 to 10 mL on low heat hot plate (usually two days).
3. Transfer with a pipette to the planchet.
4. Rinse beaker one or two times with acid solution and transfer to planchet.
5. Dry planchet.
6. Determine crud weight.
7. Analyze on beta counter - 100 minutes count time.
8. Calculate results applying correction factor for weight of crud.